

Homework 3: Canonical ensemble (continued) and radial distribution function

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Due: October 2, 2019

1. (Computational) Fill in the missing pieces in the notebook within the rdf folder on the course github:
<https://github.com/hockyg/chem-ga-2600/>
This will demonstrate how to compute a radial distribution function ($g(r)$) for somewhat realistic simulation data.

When finished, download with File->Download As->ipynb so you have a copy. Upload this file in response to the form your received by email.

2. *Ideal gas of molecules* (Adapted from Tuckerman problem 4.12). If you have N identical non-interacting molecules (each with n atoms) in a box, the total partition function factorizes,

$$Q(N, V, T) = \frac{q(n, V, T)^N}{N!} \quad (1)$$

Moreover, the single molecule partition function $q(n, V, T) = Vf(n, T)$, where f is a function that only depends on the number of atoms and the temperature.

Now suppose that the system contains different types of molecules, this factorization still works. For example, with 2 types, A and B ,

$$Q(N_A, N_B, V, T) = \frac{q_A(n_A, V, T)^{N_A}}{N_A!} \cdot \frac{q_B(n_B, V, T)^{N_B}}{N_B!} \quad (2)$$

- (a) An example chemical reaction might be



The Helmholtz free energy A is now a function of V, T , and all 4 N 's. Let there be a variable called λ which is the reaction extent. Then $dN_A = a d\lambda$,

$dN_B = b d\lambda$, $dN_C = -c d\lambda$, and $dN_D = -d d\lambda$. At chemical equilibrium, A is at a minimum, which means that $dA/d\lambda = 0$.

Show that at equilibrium with fixed V and T ,

$$a\mu_A + b\mu_B - c\mu_C - d\mu_D = 0, \quad (4)$$

where chemical potentials of each species are defined like:

$$\mu_A = -k_B T \frac{\partial \ln Q(V, T, N_A, N_B, N_C, N_D)}{\partial N_A} \quad (5)$$

Hint: This should follow very directly from writing out the chain rule for dA .

- (b) By plugging in for Q in the 4 equations like Eq. 5 and substituting this in to Eq. 4, show that you get the following relationship

$$K(T) = \frac{\rho_C^c \rho_D^d}{\rho_A^a \rho_B^b} = \frac{(q_C/V)^c (q_D/V)^d}{(q_A/V)^a (q_B/V)^b}, \quad (6)$$

where $\rho_A = N_A/V$, etc. Hint, you may have to use Sterling's approximation. Do you see why both the middle and right fractions are functions of only temperature?

- (c) Using the definition of the Helmholtz free energy and the formula for Q with 4 different species, show that the Helmholtz free energy A can be written as $A_{total} = A_A + A_B + A_C + A_D$. What is the equation for A_X , that is, the contribution to the Helmholtz free energy from species X .
- (d) The pressure in the canonical ensemble can be obtained by the formula $P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$. The partial pressure of species X can be expressed similarly as $P_X = -\left(\frac{\partial A_X}{\partial V}\right)_{N,T}$, where A_X was defined in the previous part. Given this definition, find the relationship between $K(T)$ above and

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad (7)$$

3. *Deriving the Canonical Ensemble from the perspective of Maximum Entropy.* Consider a system with N possible states each having energy ϵ_i . One definition we read for the entropy is the Gibbs entropy, $S = -k_B \sum_{i=1}^N p_i \ln p_i$, where p_i is the (unknown) probability that system is in state p_i .

By definition, $\sum_{i=1}^N p_i = 1$, and the average energy \bar{E} is a constant, with $\bar{E} = \sum_{i=1}^N \epsilon_i p_i$. Note that the Gibbs entropy is strictly positive since $0 < p_i < 1 \Rightarrow -\ln p_i > 0$.

A question we could ask is, which set of $\{p_i\}$ maximize the Gibbs entropy subject

to the constraints $\sum_{i=1}^N p_i = 1$ and $\bar{E} = \sum_{i=1}^N \epsilon_i p_i$. To do this, we can use the method of undetermined Lagrange Multipliers. If you don't know what this is, you should read about it a little on your own. The upshot is, we have to maximize the quantity:

$$L = -k_B \sum_{i=1}^N p_i \ln p_i - \alpha \sum_{i=1}^N p_i - \beta \sum_{i=1}^N \epsilon_i p_i, \quad (8)$$

where α and β are undetermined variables.

- (a) Find where L is maximum as a function of an arbitrary p_k by solving $\frac{dL}{dp_k} = 0$ for p_k , where the p 's are considered all independent variables.
- (b) Use the fact that $\sum_{i=1}^N p_i = 1$ to eliminate one of the unknown variables. Your expression for the probabilities should look familiar.
- (c) Based on what you know about the Canonical ensemble, express this β in terms of a familiar thermodynamic variable.
- (d) Optional extra part: what happens if we don't include the constraint on the average energy? What ensemble does this correspond to?